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Research papers

Stream water quality affected by interacting hydrological and biogeochemical processes in a riparian wetland

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ABSTRACT

Riparian wetlands as both hydrological and biogeochemical hot spots often have a major impact on the release of solutes from headwater catchments. Numerous studies give some evidence of a rather complex interplay of hydrological and biogeochemical processes that is still poorly understood. This study seeks to address this challenge using a multivariate solute concentration data set from a small riparian headwater wetland. First, a non-linear variant of the Principal Component Analysis (Isomap) was performed in a preceding study to identify prevailing biogeochemical processes controlling water chemistry. Second, the scores of the components of the stream draining the wetland were subjected to a cluster analysis to identify typical biogeochemical patterns for different biogeochemical and hydrological boundary conditions.

Four different clusters could be identified, which roughly followed a seasonal pattern, although modified by hydrological boundary conditions in the short-term. During the first three months of the year, Cluster 3 prevailed, indicating a discharge of rather unaltered shallow to mean depth groundwater. Cluster 3 was increasingly replaced by Cluster 2 and then subsequently by Cluster 1, indicating increasingly anoxic conditions, increasing denitrification and desulphurization, and increasing decomposition of organic carbon reflecting increasing biological activity and increasing water residence time within the wetland. However, stream water during stormflow after extended periods of low groundwater level in the second half of the growth season exhibited a very distinct pattern, represented by the fourth cluster. It indicated strong oxic conditions causing enhanced oxidation of sulphides, a corresponding decrease in pH values, and a substantial increase in the concentration of alkaline earth ions, manganese and in electric conductivity during the dry period.

It is concluded that temporal variations in stream water chemistry clearly reflected the intensity of biological activity in the wetland, interacting with water table dynamics. Our results provide strong evidence for major effects of single extreme events like drought periods which are expected to become more frequent because of climate change.

1. Introduction

Riparian wetlands are transition zones between the unsaturated zone, groundwater, and surface water (Casey and Klaine, 2001; Zhao et al., 2009), and are characterized by substantial nutrient and contaminant retention capacities (Fisher and Acreman, 2004). Solute concentration in wetland groundwater and adjacent streams often exhibits remarkable temporal and spatial variance due to varying contributions of soil solution, shallow and deep groundwater, as well as highly heterogeneous patterns of biological and hydrochemical processes within the respective catchment (e.g. Emmett et al., 1994; Kerr et al., 2008; Kull et al., 2008). Processes in the riparian wetlands often superimpose the influence of the hill slope area of the catchment upon surface water quality (Hooper, 2001; O'Brien et al., 2013; Piatek et al., 2009; Prior and Johnes, 2002). A change in biogeochemical processes in the riparian wetlands, e.g. because of increasing intensity and frequency of hydrological extreme events (long dry periods, heavy rainstorms), predicted to become more frequent because of climate change, will thus be likely to affect stream water quality directly (Emmett et al., 1994; Kull et al., 2008; Szkokan-Emilson et al., 2013; Watmough and Orlovskaya, 2015).

The importance of storm events for solute export has been documented in numerous studies (Mitchell et al., 2006; Neal et al., 2006; Raymond and Saiers, 2010; Ulen, 1995). Especially in small

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catchments, a significant amount of annual stream runoff occurs during single runoff events, accompanied by a change of surface water quality within a few hours (Kirchner, 2003).

Systematic shifts of stream water solute concentration during stormflow periods were often ascribed to hydrological processes like changes in water flow paths (Christophersen et al., 1982; Davies et al., 1992; Hagedorn et al., 2000; Lyon et al., 2011). The latter may be due to changes in riparian wetland water table depth, leading to different types of runoff events (Bechtold et al., 2003; Emmett et al., 1994; Inamdar et al., 2008; Kerr et al., 2008). This approach implies that the chemical composition within a single water flow path does not change with regard to time and space, which presumably holds only at the time scale of single stormflow periods. Consequently, the processes causing chemical signatures in runoff are still poorly understood (Aubert et al., 2013b; Dhillon and Inamdar, 2014; Kirchner, 2003).

In contrast to this hydrological perspective, biogeochemists study wetland processes at the time scale of weeks or months, and tend to ignore changing hydrological conditions and boundary fluxes, with the exception of changing groundwater levels. The focus of those studies is on internal processes and not on relating them to output fluxes via the discharging stream (Knorr et al., 2009; Pennington and Watmough, 2015; Reiche et al., 2009). Thus, little is known about the interplay between hydrological and biogeochemical processes in riparian wetlands. So far, various studies have provided anecdotal evidence: Sulphate, e.g., was found to be exported episodically after summer droughts due to oxidation of reduced sulphur (S) compounds (Eimers et al., 2007; Inamdar et al., 2008; Tipping et al., 2003; Zhang et al., 2010). The modelling study by Frei et al. (2012) illustrated how small scale spatial heterogeneity of flow paths and biogeochemical processes could yield a complex pattern of stream solute concentration during stormflow.

Various studies elucidated the interplay between hydrological and biogeochemical processes affecting solute export from riparian wetlands (Arnold et al., 2015; Piatek et al., 2009; Vidon et al., 2014), including fluctuating climatic conditions (Kull et al., 2008), seasonal factors (Muller and Tankéré-Muller, 2012) including seasonal hydrologic events (Kerr et al., 2008), changes in the water flow pathways (Christophersen et al., 1982; Kerr et al., 2008; Mitchell et al., 2006), antecedent moisture conditions (Inamdar et al., 2009; Mitchell et al., 2006), redox processes (Kerr et al., 2008), available solute concentration in the wetland (Piatek et al., 2009), dilution of solutes (Inamdar et al., 2009), and the flushing of solutes after drought periods (Emmett et al., 1994; Szkokan-Emilson et al., 2013). Aubert et al. (2013b) investigated seasonal patterns of flood-induced variability in stream water chemistry by using a probabilistic clustering method. Inamdar et al. (2013) highlighted the need to recognize temporal shifts in the end-member chemistry as a function of catchment wetness to better characterize catchment flow paths and mixing responses. Knorr (2012) emphasized the importance of both hydrological and redox conditions in the wetlands for solute export in the catchment of this study.

Water resources management must consider spatial and temporal patterns of biogeochemical and hydrological processes for assessing the impact of climate and land use change on solute export. Management practices are often based on results from biogeochemical modelling. However, non-linear interactions between hydrological and biogeochemical processes in catchments render the understanding and prediction of long-term behaviour of surface water quality difficult. Thus, the objective of this study was to elucidate the interplay between biogeochemical and hydrological processes and to weight their respective relevance with regard to water quality in the receiving stream. It was hypothesized that the temporal patterns of wetland stream water chemistry were not related to changes in hydrological flow paths but that stream water chemistry reflected varying antecedent biogeochemical boundary conditions in the wetland. However, it was assumed that biogeochemical processes in the wetland were affected by the groundwater level which determined the degree of anoxia in the uppermost soil layer.

This study builds upon a preceding study by Weyer et al. (2014). Prevailing biogeochemical processes in the Lehstenbach catchment were identified in a comprehensive data set comprising soil solution, groundwater, spring water, and stream water solute concentration data from upslope and wetland sites using the Isomap approach (Isometric Feature Mapping; Tenenbaum et al., 2000). Isomap can be considered a non-linear variant of Principal Component Analysis (PCA). As different observables of the multivariate water quality data set exhibited numerous, although partly non-linear relationships, a large fraction of the variance could be represented by a small number of Isomap components. As these components were independent, they were used to identify the prevailing biogeochemical processes. In addition, the component scores were used as a proxy for quantifying the intensities of the respective biogeochemical processes.

This study focused on a subset of the data set used by Weyer et al. (2014), comprising data from 280 samples taken in a stream that drained a small wetland in the Lehstenbach catchment. In addition to solute concentration values, the Isomap component scores of the samples as a quantitative assessment of the intensity of the prevailing processes were included. This study aims at a better understanding of the observed pronounced temporal variability of stream water quality, i.e., at differentiating between biogeochemical and hydrological drivers. To that end, a Cluster Analysis (CA) was used to classify stream water samples. As that classification was based on the scores of the independent Isomap components, it does not only solve the problem of collinearity as is often recommended (Fröhlich et al., 2008; Menció and Mas-Pla, 2008; Woocay and Walton, 2008). Moreover, it allowed interpreting the clusters in terms of intensities of identified biogeochemical processes which would not be possible by using solute concentration data. A time series of cluster assignment of the stream water samples was related to the respective meteorological and hydrological boundary conditions, and conclusions were drawn with respect to the interplay between biogeochemical and hydrological processes. In addition, the classification of stream water samples was compared to the well-known Schöller- and Piper-classification of water samples (Piper, 1944; Schoeller, 1962). Finally, implications for explaining temporal patterns of single solutes in stream water quality are discussed.

2. Data and methods

2.1. Data

The current investigation involved samples of a wetland stream within the Lehstenbach watershed (50°08′N and 11°52′E) in the Fichtelgebirge Mountains in southeast Germany. Extensive monitoring programs have been run in this catchment since the end of the 1980s, including several studies on groundwater and stream water chemistry.

The watershed area is 4.19 km^2 and elevation ranges from 690 to 877 m a.s.l. (Fig. 1). The bedrock consists of variscan granite of two different facies (Stettner, 1964), which show very similar mineralogical compositions. Significant differences between the two facies with respect to geochemistry (Weyer et al., 2008) or hydrogeology (Partington et al., 2013) have not been observed. The thickness of the regolith is up to 40 m and more. Dystric cambisols and podzols predominate. In the riparian zone, fibric histosols and dystric gleysols are present, representing about one-third of the watershed area. The area is drained by a dense network of natural streams and artificial channels. Dense Norway spruce stands (*Picea abies*) cover more than 95% of the watershed area. Annual mean air temperature is 5.8 °C, annual mean precipitation is between 950 and 1250 mm. Annual mean runoff of the Lehstenbach stream, i.e. the catchment outlet, was 470 mm during the period from 1991 to 2001 (Lischeid et al., 2010). Snowpack usually develops in December or January, and final snowmelt occurs in March or April. The site has been severely impacted by sulphate deposition that peaked in the 1970s and has decreased by more than 80% since

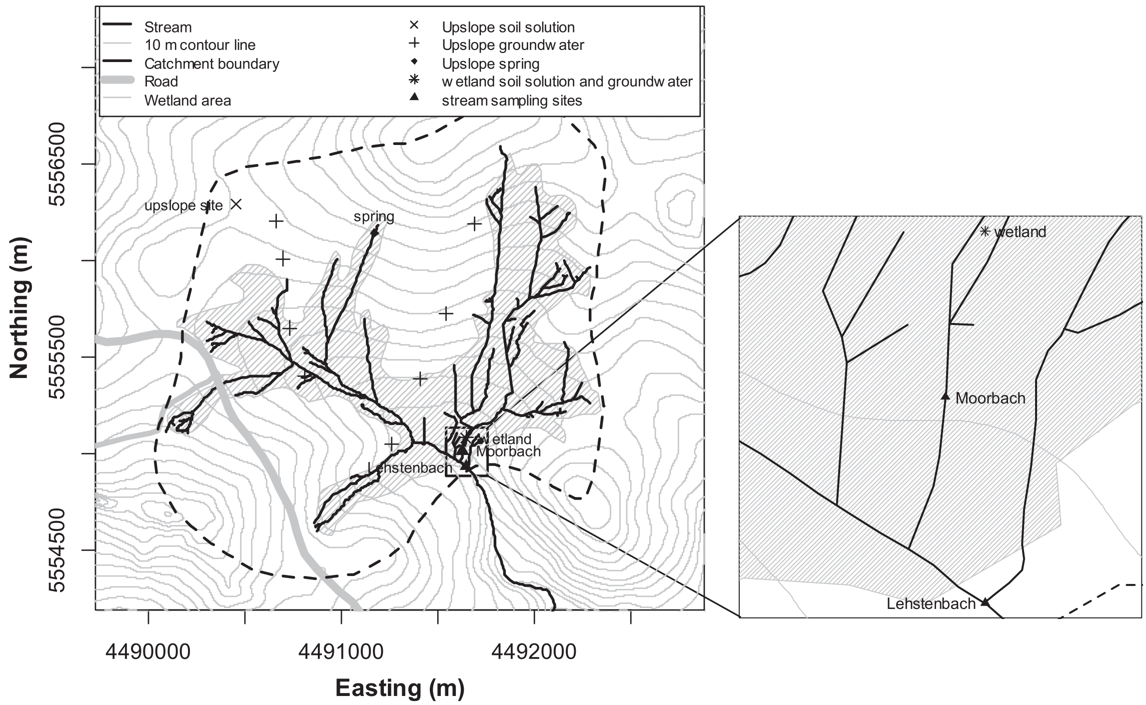

Fig. 1. Map of the Lehstenbach watershed. Gauss-Krüger coordinates [m] are given at the axes. Moorbach: Moorbach stream; Lehstenbach: Lehstenbach stream.

then (Matzner et al., 2004).

This study focused on the ephemeral Moorbach stream that drains the slightly acidic Schlöppnerbrunnen fen, later referred to as “wetland”, near the catchment outlet (Fig. 1). The fen area is 0.08 km^2. The thickness of the peat layer on top of the mineral soil ranges between 30 and 70 cm (Reiche et al., 2009). The runoff of the Moorbach stream is exclusively composed of wetland waters, i.e. by waters that originate in the wetland or by groundwater that has passed through the wetland area. Discharge of the Moorbach stream was between 0 and 4l/s during most of the study period. During discharge peaks, up to 439l/s were observed. Three plots of 7.2 m × 5 m each were subjected to two drying/rewetting experiments from August to September 2006, and from May to July 2007 (for more details see Reiche et al., 2009). The rest of the wetland was not manipulated.

More than 600 stream water samples from the Moorbach stream were taken between April 2005 and November 2007 with an ISCO automatic sampler at daily intervals. No samples could be taken during the frost period or when the Moorbach stream fell dry. Samples were filled in thoroughly-rinsed polyethylene bottles in the automatic sampler. The filled bottles were at least collected every three weeks and directly transported to the central laboratory of the Bayreuth Center of Ecology and Ecological Research (BayCEER). In all collected samples, electric conductivity (EC) and pH values were measured directly after collection with a TetraCon® 325 conductivity cell (WTW), and with a SenTix® 41–3 electrode (WTW), respectively.

Initially, from April to June 2005, daily stream water samples were analysed. Afterwards, only samples taken during runoff events were selected according to stream discharge and electric conductivity values. In total, 280 stream water samples were selected to be analysed as described below.

Selected water samples were filtered through a cellulose-acetate-membrane filter with 0.45 µm pore size. They were stored in thoroughly-rinsed polyethylene bottles in the dark at 2 °C until further analysis. The element concentrations of aluminium (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), total sulphur (S) and silica (Si) were analysed by ICP-OES (Varian Vista-Pro CCD Simultaneous). Chloride (Cl), nitrate (NO_3) and sulphate (SO_4) were analyzed using ion chromatography (IC Dionex DX 500), dissolved organic carbon (DOC) by temperature combustion and subsequent determination of carbon dioxide (CO_2) (Analytik Jena Multi N/C 2100F), and ammonium (NH_4) by Flow Injection Analysis (FIA-LAB by MLE). Quality assurance of the data was performed prior to this study by the central laboratory of the Bayreuth Center of Ecology and Ecological Research (BayCEER).

2.2. *Methods*

Data handling, statistical analysis and plotting were performed using the R environment (R Development Core Team, 2006). The Cluster Analysis was performed with the package “cluster” (Maechler et al., 2007). The packages “Hmisc” (Harrell et al., 2014), “multcompView” (Graves et al., 2012) and “hydrogeo” (English, 2017) were used to produce the graphics.

2.2.1. *Statistical analysis*

Different (non-linear) multivariate statistical methods were used sequentially to analyse water solution data. A global flowchart of the different steps of statistical analysis is shown in Fig. 2.

2.2.1.1. Preceding analysis of water quality data. The data set used for this study is a subset of the original data set used by Weyer et al. (2014), comprising soil solution, groundwater, spring water and stream water samples from various sites within the catchment, including upslope soils.

Weyer et al. (2014) applied a non-linear version of a Principal Component Analysis, the Isometric Feature Mapping (Isomap) approach, to the original data set in order to identify the prevailing biogeochemical hot spots along different subsurface flow paths from the soil surface to the catchment outlet. The approach reduced the dimensionality of the original data set, comprising 1686 single samples with 16 parameters each, down to three components (Fig. 2). The three components explained 89% of the total variance (48%, 30%, and 11%, respectively). The first component was positively correlated with SO_4, NO_3, Mn, K, Mg and Ca concentrations and electric conductivity, but was negatively correlated with Fe and Si concentrations and pH values. The second component was associated with high DOC, Fe, and Al

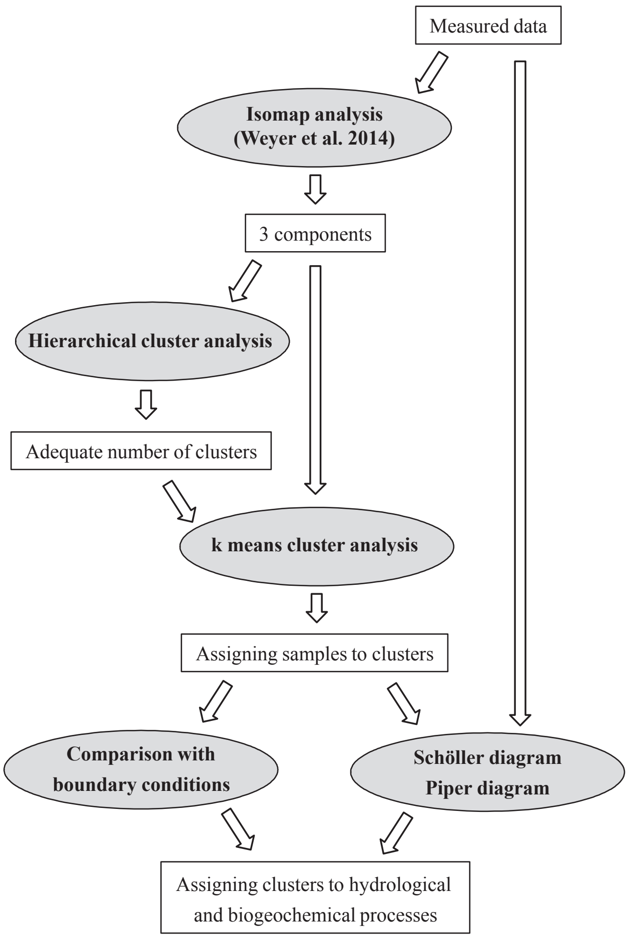

Fig. 2. Flowchart of the approach followed using different methods (grey shaded ellipses).

concentrations, but low SO_4 and Na concentrations and low pH values. The third component was characterized by positive loadings of Cl, Si, NH_4, K, Na, and pH values and negative loadings of Al, and SO_4. The first component was ascribed to redox processes, the second to acid-induced podsolization, and the third to weathering processes in the subsurface (Weyer et al., 2014). Every sample of the data set was assigned a score of the respective components as a quantitative measure for the strength of the respective effects on that water sample. It could be shown, that for all three components the uppermost 10 cm of the riparian wetland as well as the uppermost 1 m of upslope soils played a crucial role for solute concentration in the receiving streams.

For this study, a subset of data from a small wetland stream was used as described above. It was assumed that the three biogeochemical processes identified with the Isomap approach prevailed in the whole catchment, including the wetland site. Thus, the Cluster Analysis was performed on the scores of the first three components of the Moorbach stream samples rather than on the values of the 16 solutes. This was done as it was recommended to perform a Cluster Analysis on whitened data in order to not give too much weight to parameters that were strongly correlated to each other. On the other hand, the original data set used by Weyer et al. (2014) contained chemical information from various water sources, including soil solution and groundwater from upslope and wetland sites. It was therefore expected, that it would reflect, to a larger degree, processes that are more visible in other parts of the catchment, like acid-induced podsolization. In addition, results of this study can be directly related to that of the Weyer et al. (2014) study.

2.2.1.2. Cluster Analysis (CA). A Cluster Analysis was performed using the scores of the first three Isomap components of 280 Moorbach stream water samples selected from the original data set used by Weyer et al. (2014) in order to group water samples that were influenced by the same biogeochemical processes (Fig. 2). Cluster Analysis aims at classifying samples according to a similarity measure and a grouping algorithm. Agglomerative hierarchical cluster analysis uses the distance between samples as a measure of similarity (Vega et al., 1998). At different distances, different clusters will form, which can be represented using a dendrogram. In contrast, the k-means clustering aims at finding the cluster centroids for a given number of clusters. Objects are assigned to the nearest cluster centroid by minimizing the squared distances from the latter.

The Isomap scores of the Moorbach stream water samples were first normalized to zero mean and unit variance for each component separately. First, a hierarchical clustering (agglomerative nesting) was performed (Fig. 2) to assess an adequate number of clusters using the knee criterion (Dubes and Jain, 1979; Tibshirani et al., 2001), i.e., a compromise between a minimum number of clusters and a minimum sum of squared errors of assignment to clusters. The sum of squared errors is defined as the sum of the squared distance between each member of a cluster and its cluster centroid. Using the number of clusters found in this manner, in a second step, a k-means clustering was performed (Fig. 2). The centroids of each cluster and the distances between the observations and the cluster centroids were calculated. Observations with a smaller distance to another centroid than to the own centroid were then relocated to the other cluster in an iterative procedure.

The Cluster Analysis yielded a classification of the 280 water samples. In a next step, the clusters were analysed for significant differences with respect to component scores as well as to solute concentration. To that end, the Wilcoxon test with Bonferroni correction for multiple testing was used for pairwise comparison between different clusters. In contrast to, e.g., the well-known *t*-test, the applied test can handle strongly differing numbers of samples per group and does not require any specific distribution. Level of significance was 5% in all cases.

The same test was used to test for significant differences between the clusters with respect to the boundary conditions of the sampling dates. Boundary conditions were characterized by daily mean values of discharge, groundwater level, precipitation, air temperature and Julian day of the sampling dates. Discharge was logarithmised after adding a constant offset of 1l/s in order to avoid logarithmising of zero values. Precipitation was summed up for a period of 30 days before each sampling date, respectively. In addition, a rough proxy for water residence time in the riparian wetland was used by determining the number of preceding days since the last exceedance of a discharge threshold of 1l/s. Determination of that proxy variable was possible only for periods without data missing from the hydrograph. Thus, part of the water samples could not be assigned a value of that proxy variable.

For visualization of differences between clusters, box-percentile plots were used. They can be regarded as approximations of the probability density of the respective variable, but rotated by 90°. More precisely, the width of the figure is proportional to the percentile of that height up to the 50th percentile. Above the 50th percentile, the width is proportional to 100% minus the percentile. Thus, the width at any given height is proportional to the percent of observations that are more extreme in that direction. In addition, the first, second, and third quartile is marked by horizontal lines (Esty and Banfield, 2003).

2.2.2. Schöller and Piper classification of stream water samples

To allow for comparison with standard methods of multivariate water quality visualisation, stream water quality and cluster means were plotted in Schöller and Piper diagrams (Fig. 2). For the Schöller diagram, mean values, the 10th and the 90th percentiles of solute concentration of the stream water samples were plotted for each of the four clusters. For the Piper diagram, charge equivalents of Ca, Mg, Na,

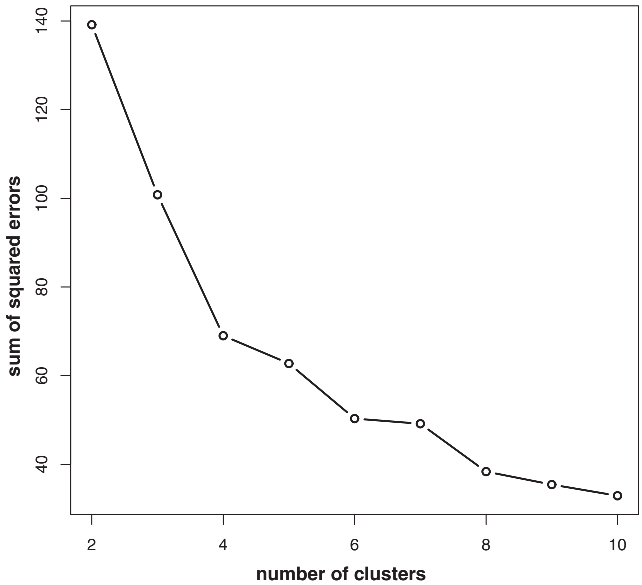

Fig. 3. Sum of squared error of cluster assignment vs the number of clusters for the last ten steps of the agglomerative cluster analysis.

K, Cl, NO_3, SO_4 and hydrogencarbonate and bicarbonate (HCO_3^- and CO_3^{2-}) were calculated. Then, the percentage of each cation and anion with respect to the total sum of cations and anions, respectively, was calculated. Stream water samples assigned to the same cluster were plotted using the same symbol in order to differentiate between the four clusters.

3. Results

3.1. Identification of clusters

The appropriate number of clusters was chosen using the sum of squared errors within a group plotted against the number of clusters (Fig. 3): at the point where the reduction of sum of squared errors with increasing number of clusters slowed down markedly. This point was found at four clusters, subsequently named Cluster 1 to Cluster 4. Each of the 280 water samples was assigned to one of these four clusters: 56 samples to Cluster 1, 101 to Cluster 2, and 93 and 30 to Cluster 3 and 4, respectively.

Fig. 4 gives the scores of the first three Isomap components, Fig. 5 shows the pH values, electric conductivity and concentration of selected solutes for each of the four clusters. Different letters a, b, c, and d denote the significantly different median values of the respective Isomap component scores and the respective variables between the respective clusters in Figs. 4 and 5, respectively. All clusters differed significantly with respect to the scores of all three components, and for most of the solutes as well, except for NH_4 (not shown). Scores of the first component increased systematically from Cluster 1 to 4, indicating increasingly oxic conditions. In contrast, scores of the second component decreased systematically, pointing to decreasing acid-induced podsolization. A different pattern was exhibited by the scores of the third component. Scores increased from Cluster 1 to 3 and decreased for Cluster 4 again (Fig. 4). Peak values for the third cluster indicated the strongest effect of weathering processes for these samples, which was typical for groundwater at greater depths (Weyer et al., 2014).

These patterns were reflected by three different groups of solutes. The first group, comprising of electric conductivity, SO_4, Ca, Mg, Mn and S (not shown) exhibited an increase from Cluster 1 to 4, similar to the scores of the first component. The opposite was true for the second group, including pH, DOC, Al and Fe, similar to the scores of the second component. The pattern of the third component was mimicked by the third group, i.e., by Si, K and NO_3. The same held for Na and Cl (not shown).

3.2. Time series and typical boundary conditions

Time series of cluster assignment of the 280 stream water samples during the 2005–2007 sampling period are shown in Fig. 6 and were compared to that of discharge and groundwater levels in the riparian wetland. In addition, Julian day and the respective meteorological and hydrological boundary conditions during sampling days are compared to cluster assignments in Fig. 7.

On average, samples were taken every 3–4 days. However, sampling intervals differed widely between one hour and 99 days, partly due to the stream occasionally drying up. In general, assignment to clusters exhibited considerable persistency: in more than 80% of all cases, consecutive samples were assigned to the same cluster. A systematic change of cluster occurrence before, during or after runoff events could not be observed. Thus, pronounced changes of stream water solute concentration could be ascribed, in the first place, to slowly modifying conditions within the wetland rather than to short-term hydrological processes.

Time series of assignment to clusters roughly followed a seasonal pattern, although with considerable modification within and between the years. Samples taken during the first three months of the year were exclusively ascribed to Cluster 3 (Figs. 6 and 7). Correspondingly, air temperature during sampling was the lowest, groundwater level the highest, and time since last preceding discharge peak (as a rough proxy for water residence time within the wetland) the shortest compared to all clusters (Fig. 7).

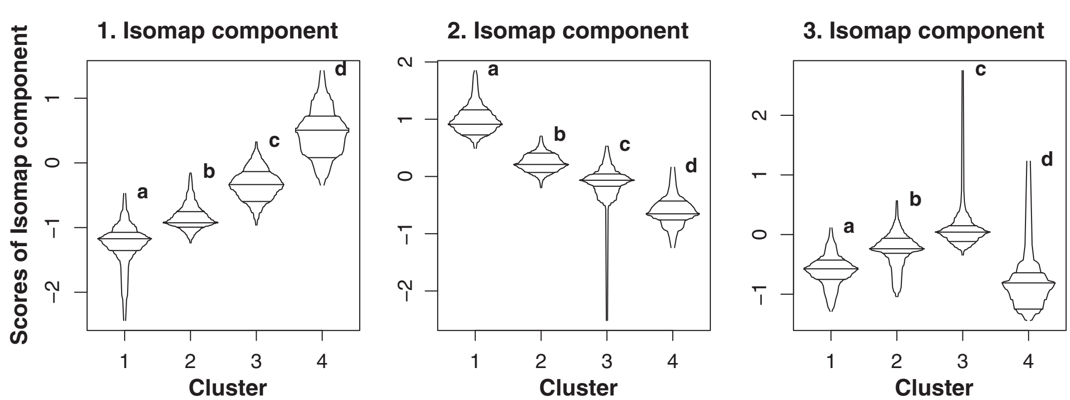

Fig. 4. Box-percentile plots of the scores of the first three Isomap components (1st, 2nd, 3rd) for each of the four clusters. The width at any given height is proportional to the percent of observations that are more extreme in that direction (Esty and Banfield, 2003). Horizontal lines mark the median, 25th and 75th percentiles. Significant differences between the clusters are denoted by different letters a, b, c and d.

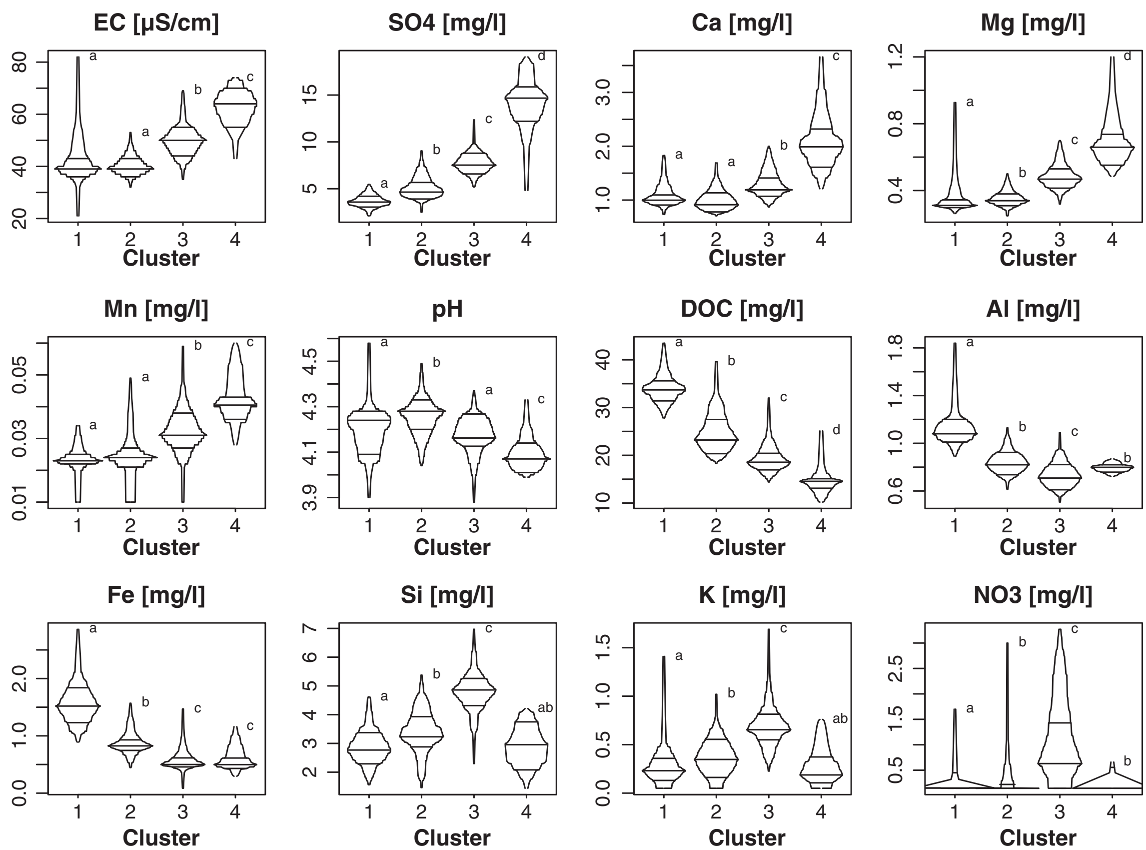

Fig. 5. Box-percentile plots of the concentration of different solutes, electric conductivity (EC) and pH-values for each of the four clusters. Significant different distributions of the respective variables between the respective clusters are denoted using different letters a, b, c and d.

Later in the year, Cluster 3 was subsequently replaced by Cluster 2, and then by Cluster 1 (Fig. 6), along with rising air temperature and lower groundwater level (Fig. 7). Likewise, cumulative precipitation for a 30 day-period was the lowest for Cluster 2. Correspondingly, scores of the first component decreased, indicating increasingly anoxic conditions. Groundwater level and cumulative precipitation for Cluster 1 was significantly higher than for Cluster 2, representing recovering of the groundwater level after periods of moderate groundwater level drawdown (less than 15 cm). Increasing scores of the second component pointed to increasing effects of acid-induced podsolization, and decreasing scores of the third component to decreasing effects of weathering processes. Thus, stream water became increasingly dissimilar compared to groundwater solute concentration.

Four samples in early July 2005, and another 26 samples in 2006, mostly in August and October, were assigned to Cluster 4 (Fig. 6). During all of these three periods, groundwater level was low (Fig. 7), but recovered from preceding extensive drawdown (Fig. 6). Correspondingly, water residence time within the riparian wetland was on average the largest for Cluster 4 (Fig. 7). Cumulative precipitation was intermediate. In contrast to 2005 and 2006, there was no similar drawdown of groundwater level after mid-May in summer 2007, and no sample was assigned to Cluster 4 (Fig. 6).

Although samples of Cluster 4 usually followed immediately after those of Cluster 1 or 2 (Fig. 6), they differed to a maximum extent with respect to scores of components 1 and 2 (Fig. 4), and with respect to most solutes (Fig. 5). Scores of the first and of the second component of Cluster 4, compared to those of Cluster 1 (Fig. 4), indicate that this change came along with a drastic reoxidation and a strong decrease of acid-induced podsolization. Depending on the respective hydrological conditions, Cluster 4 was then either rapidly replaced by Cluster 1 (2005) or by Cluster 2 or 3 (2006) (Fig. 6).

Cluster occurrence did not vary between base flow and storm flow conditions as long as the water table was near the soil surface (runoff events April and May 2005, January 2007; Fig. 6). Furthermore, there seemed to be no dependence of cluster occurrence on the magnitude of the runoff event. For example, discharge of the Moorbach stream after two comparable periods of extensive groundwater level drawdown (more than 20 cm) was 1.76 l s^{-1} and 20.22 l s^{-1} in July 2005 and October 2006, respectively, with a comparable cluster occurrence. Similarly, discharge of the Moorbach stream after three periods of moderate groundwater level drawdown (less than 15 cm) was near 0 l s^{-1}, 43.10 l s^{-1} and 12.84 l s^{-1} in June 2005, June 2007 and August 2007, respectively, also with a comparable cluster occurrence. Correspondingly, there was no significant difference between average discharge values for Cluster 1 and 4 (Fig. 7), the most differing clusters with respect to water chemistry (Figs. 4 and 5).

The two drying/rewetting-experiments conducted from August to September 2006 and from May to July 2007 in three of the six sampling plots in the wetland under study did not seem to have an influence on stream water quality. Indeed, cluster occurrence in the Moorbach stream water samples taken during and after the experiments could be explained by naturally occurring hydrological conditions.

3.3. *Schöller and Piper classification of cluster means and stream water samples*

All of the four clusters showed comparable patterns in the Schöller diagram (Fig. 8). Highest mean concentrations were observed for SO_4, followed by Si and Na. Lowest mean concentrations were observed for Mn and NH_4. Mean solute concentrations differed for the different clusters with respect to Ca, Mg, Fe, NO_3, SO_4 and DOC. Corresponding to the results of the CA, Cluster 4 showed the highest mean SO_4 concentration.

Using the Piper diagram (Fig. 9), stream water samples can be

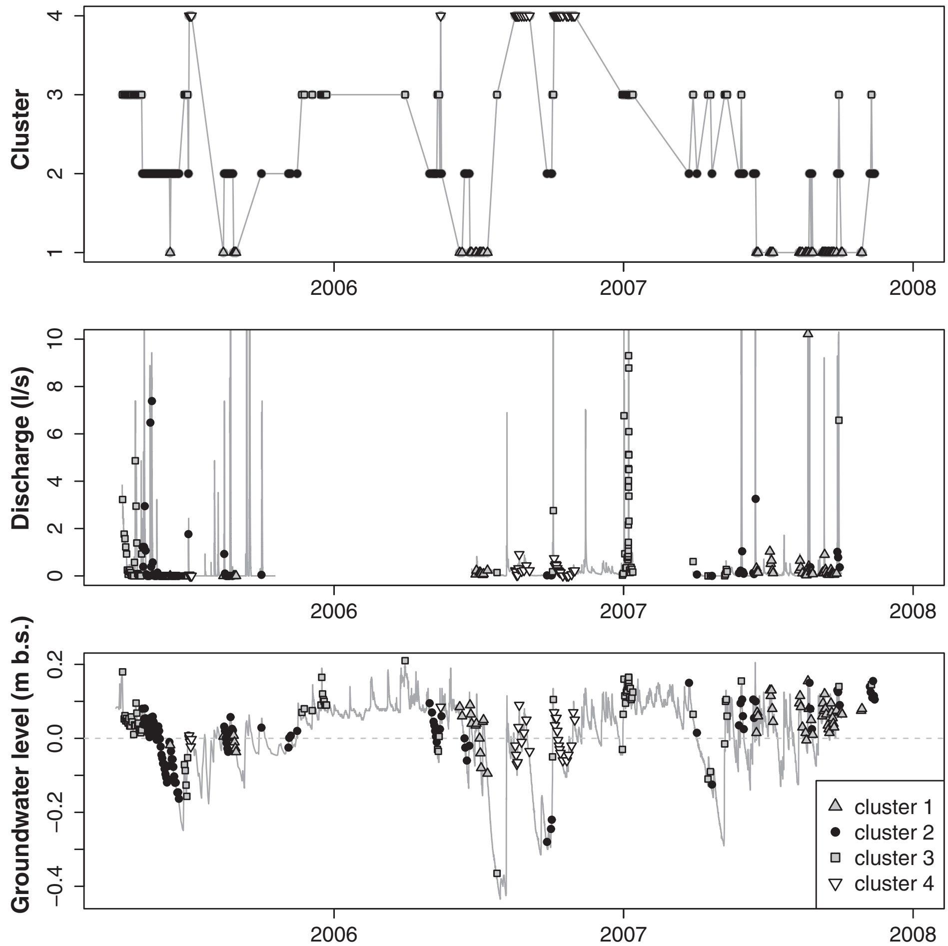

Fig. 6. Time-series of assignment of water samples to the four clusters, discharge of the Moorbach stream, and groundwater level below surface in the wetland.

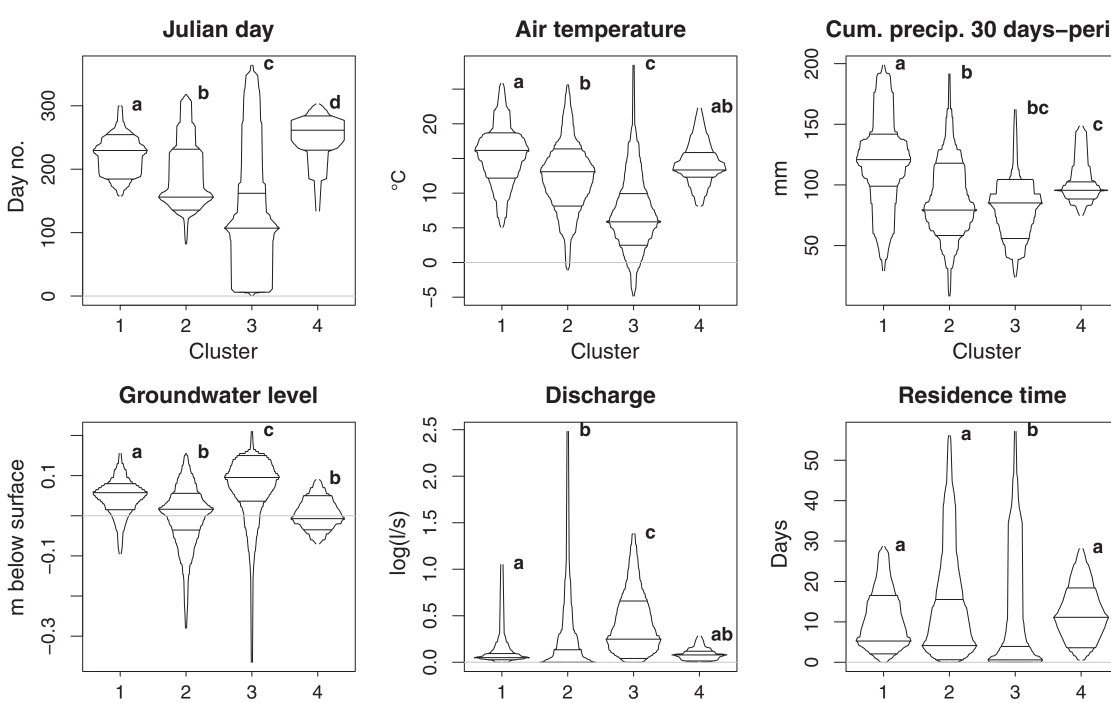

Fig. 7. Box-percentile plots of candidate predictor variables for each of the four clusters in order to characterize the boundary conditions of the sampling dates. Significant differences between the respective clusters are denoted by different letters a, b, c and d.

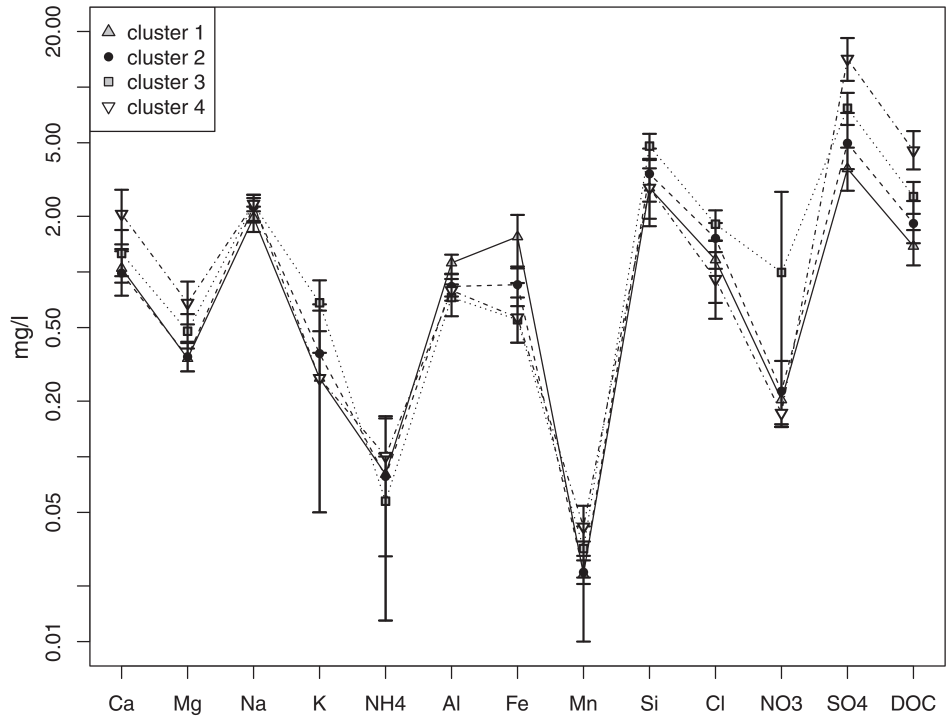

Fig. 8. Schöller diagram of mean concentrations (mg/l) of the wetland stream water samples assigned to the four clusters. Lower and upper limit of the error bars represent the 10th and the 90th percentiles.

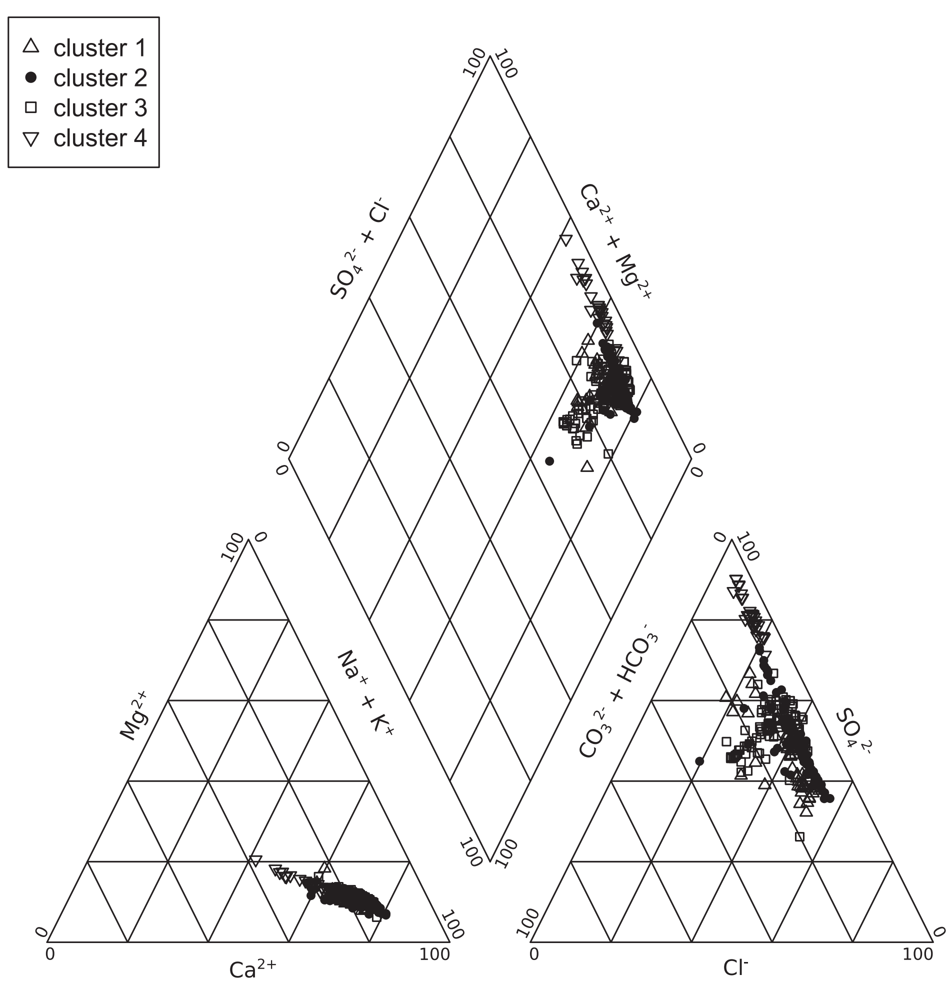

Fig. 9. Piper diagram of the 280 wetland stream water samples assigned to the four clusters.

classified as sodium-potassium type and as chloride to sulfate type. Water samples assigned to Cluster 4 showed considerably higher SO_4 and Ca, but lower Cl concentrations than water samples assigned to the other clusters. In contrast, water samples assigned to Cluster 3 showed remarkably lower SO_4 concentrations but higher CO_3^{2-} + HCO_3^{-} concentrations. Water samples assigned to Cluster 1 showed the lowest SO_4 concentrations but higher Cl concentrations compared to the other water samples.

4. Discussion

This study aimed at elucidating the interplay between internal biogeochemical processes in a riparian wetland and hydrological processes at the time scale of days to months. The samples are regarded as representative samples of the wetland water being mobilized especially during single runoff peaks. Clustering necessarily implies ignoring within-cluster variability and overemphasizing differences between clusters. Although the knee criterion, applied here for selection of an adequate number of clusters, is widely accepted (Dubes and Jain, 1979; Tibshirani et al., 2001), any clustering of a presumably more or less continuous data set is, to a certain degree, arbitrary. Consequently, assignment of single samples to certain clusters can always be questioned. However, clustering can help identify certain structures in large data sets.

In this study, samples were clustered based on the scores of an Isomap analysis that determined the independent components. Each of these components had been interpreted as a quantitative measure of the strength of the effect of single processes in a preceding study (Weyer et al., 2014). However, this interpretation is not a necessary prerequisite for this study and the inferences drawn from the results. As has been illustrated in Fig. 5 clusters can be equally well analyzed and interpreted in terms of solute concentration. Different clusters can be distinguished in the Piper and the Schöller diagrams as well (Figs. 8 and 9), although observable differences between clusters in the two diagrams were less clear compared to the classification by the CA. However, in general, results of the Piper and Schöller classification were in line with the results of the CA. For example, Clusters 1, 3 and 4 could be distinguished in the Piper diagram, mainly with respect to Ca and SO_4 (Fig. 9).

The sampled stream had its only source in the wetland. The wetland is a discharge area of groundwater that had been recharged further uphill (Partington et al., 2013). This groundwater is characterized by very low scores of the second Isomap component, that is, low acid-induced podsolization, and high scores of the third component, indicating strong effects of weathering (Lischeid and Bittersohl, 2008; Weyer et al., 2014). Temporal variability of these effects is very low. Thus, taking groundwater solute concentration as a background, any modification observed in the wetland stream has to be ascribed to wetland internal processes. The stream was sampled roughly 50 m downstream from its source. Thus, in-stream processes do not need to be accounted for, due to a very short residence time within the stream.

In the following, the four different clusters are first discussed, emphasizing the interplay between the typical biogeochemical processes represented by the clusters with the different hydrological and seasonal boundary conditions, respectively. Corresponding to the results section, clusters are discussed in chronological order of occurrence during the course of the year. Then, implications for the temporal variability of stream water chemistry during runoff events and for the temporal patterns of single solutes in the Moorbach stream water are discussed.

4.1. Cluster 3: Discharging unaltered groundwater

In winter and early spring, when the temperatures and the microbial activity are low, only Cluster 3 was observed (Fig. 6). Anoxic redox processes (first component) seemed to play a minor role, reflected by low negative mean component scores, although the wetland is completely water saturated due to low evapotranspiration. Obviously, microbial oxygen consumption and subsequent reduction of the redox potential in the wetland was very low in winter and early spring due to low temperatures and did hardly alter the quality of the groundwater discharging into the wetland stream. In addition, residence time of water within the wetland was the shortest for samples of Cluster 3 (Fig. 7), which adds to the effect of slow kinetics of biogeochemical processes during the winter months. Correspondingly, the highest NO_3 and relatively high SO_4 and DOC values were observed in the Schöller diagram (Fig. 8).

4.2. Clusters 2 and 1: Enhanced microbial activity and anoxic conditions

Cluster 2 ranges between Cluster 3 and 1 with respect to all Isomap components and to all solutes (Figs. 4 and 5). In the Piper diagram as well, Cluster 2 is placed between Cluster 3 and Cluster 1 (Fig. 9). Cluster 2 is considered a transitional stage between the two. This holds for the temporal order of cluster occurrence as well, although with some minor exceptions (Fig. 6). Thus, both clusters are discussed in a common section.

Simultaneously with rising temperatures in spring and early summer, Cluster 3 was subsequently replaced by Clusters 2 and 1 in every year of the study period (Figs. 6 and 7). Rising air and soil temperature likely led to a considerable increase of microbial activity, and thus to more rapid kinetics of the respective processes. On the other hand, increasing transpiration lowered the groundwater level in the wetland, and thus decreased the frequency of runoff peaks. The data of another riparian wetland in the Lehstenbach catchment presented by Frei et al. (2010) illustrated the relationship between groundwater level and discharge. Decreasing frequency of runoff events in turn resulted in increased mean residence time of water within the wetland (Figs. 6 and 7). Thus, the effects of microbial activity became even more pronounced. Consequently, oxygen depletion set in, and the scores of the first Isomap component decreased, indicating increasingly anoxic conditions, as was observed in other studies as well (Kull et al., 2008; Olivie-Lauquet et al., 2001). Please note that scores of that component reflect conditions in the wetland, rather than conditions in the wetland stream, which in fact was oxic due to being exposed to the atmosphere. Instead, very low NO_3 and SO_4 concentrations in stream water samples (Fig. 5) were indicative of denitrification and desulphurication in the wetland. Anaerobic mineralization could be stimulated by regeneration of electron acceptors due to frequent fluctuations in the water table, and thus drought and rewetting events (Blodau and Moore, 2003; Deppe et al., 2010; Knorr et al., 2008; Knorr et al., 2009). Such fluctuations were observed within the uppermost 15 cm in the wetland of the study site during the period of August to September 2007, when most of the samples were ascribed to Cluster 1. Correspondingly, on average, the highest cumulative precipitation for a 30 day-period as well as a higher groundwater level for Cluster 1 compared to Cluster 2 was observed. Because SO_4 was by far the dominating anion, concentration of alkaline earth cations and of Mn in the stream decreased as well (Fig. 5). Contrary to common expectations, Mn concentration in the Lehstenbach catchment is obviously more closely related to ionic strength rather than to redox processes (Lischeid and Bittersohl, 2008). Similarly, increasing Mn concentration with increasing redox potential was observed by Frohne et al. (2011) in soils instead of the expected precipitation of Mn oxides, presumably due to an equally low pH, as in this study, and to precipitation of Mn sulphides. Increasing residence time increased the effect of other biogeochemical processes in the wetland as well. These processes are not necessarily related to temperature. Clusters 2 and 1 exhibited enhanced effects of acid-induced podsolization processes (higher mean scores of the second component) and Al-releasing weathering reactions (lower mean scores of the third component) discharging to the Moorbach stream when compared to Cluster 3. Similar observations were found by Olivie-Lauquet et al. (2001). They suggest that the microorganisms which use soil iron and

manganese oxy-hydroxides as electron acceptors catalyzed the change of redox conditions and induced an increase of DOC concentration. The close relationship between Fe-reducing conditions and DOC release corresponds to the findings of Knorr (2012) at the wetland site of our study and with the results of Lambert et al. (2013). Concomitantly, trace elements like Al adsorbed to the Fe(hydr)oxides are released (Stumm and Sulzberger, 1992; Trolard et al., 1995). These processes likely produce a chemical composition of water samples similar to that produced by acid-induced podsolization processes associated with the second component and likely add to the latter. In addition, the enhanced podsolization processes in the wetland compared to Cluster 3 could be explained by aeration of the top of the small hummocks in the wetland (cf. Frei et al., 2010). In fact, the top of the small hummocks were water-saturated during both the snowmelt period and single rainstorms, and subsequently fell dry, leading to a chemical signature comparable to that of the soil solution at upslope sites as was observed for the uppermost soil layer in another wetland of the same catchment (Lischeid et al., 2007). With respect to the third component, a high affinity of Al for DOC has been demonstrated in numerous studies (Helmer et al., 1990; Kerr et al., 2008; Olivie-Lauquet et al., 2001; Szkokan-Emilson et al., 2013). In waters with DOC $> 15\,mg\,l^{-1}$ – as was the case for the wetland and the Moorbach stream in our study – up to 100% of total Al was present as humate complexes (Viers et al., 1997). Thus, decomposition of these humate–Al–complexes could have resulted in a seasonally-variable export of both DOC and trace elements like Al from wetlands to streams. Higher Al concentration in stream water due to higher microbial activity in summer was also observed by other authors (Muller and Tankéré-Muller, 2012). To summarize, Clusters 1 and 2 seem to represent wetland waters discharging into the Moorbach stream influenced by more pronounced biogeochemical processes as compared to those influencing Cluster 3 in spring and early summer. This pattern was reflected in the Schöller classification mainly by decreasing NO_3, SO_4 and DOC and also by increasing Fe concentration (Fig. 8).

4.3. Cluster 4: rewetting after extensive groundwater level drawdown

Cluster 4 was observed after periods of extended groundwater level drawdown by more than 20 cm in summer and autumn (samples taken in early July 2005, August and October 2006; Fig. 6). The significant lower groundwater level and a significant lower antecedent cumulative precipitation (30 days period) seemed to be the most important differences as compared to Cluster 1, because there were no significant differences between these two clusters with respect to discharge, air temperature and residence time for the sampling dates (Fig. 7). In spite of that, the hydrochemical status in terms of the scores of the first two Isomap components and of most solutes (Figs. 4 and 5) differed the most between these two clusters, which was reflected in the Schöller and Piper classification as well (Figs. 8 and 9).

In 2007, not a single stream water sample was assigned to Cluster 4, although a similar drawdown of the groundwater level occurred in 2007 when compared to 2005 and 2006. However, groundwater drawdown and subsequent rewetting in 2007 occurred in early May; i.e., much earlier in the course of the year when compared to 2005 and 2006. This might indicate that microbial activity in April and in early May 2007 might not have been high enough to provide the conditions necessary for generating the stream water quality of Cluster 4. Obviously, memory effects have to be taken into account here.

Moorbach stream water samples characterized by this cluster reflected wetland water being highly influenced by oxic conditions (high scores of the first component, i.e., high NO_3 and SO_4 concentration, low Fe concentration) and by acidifying effects of historical SO_4 deposition (low scores of the second component, i.e., low DOC and Fe concentration, high SO_4 and Na concentration). Concurrently, a low influence of cation exchange or silicate weathering was observed (low scores of the third component). The results of the Piper and Schöller classification were in line with these findings (Figs. 8 and 9). Similar observations after drought periods were made, e.g., by Lamers et al. (1998), Szkokan-Emilson et al. (2013) and Watmough et al. (2016). Water level drawdown during drought periods can lead to oxidation of nitrogen (N), sulphur (S) and iron (Fe) species and to the concomitant release of protons in the upper soil layers in the wetland. Consequently, the upper soil layers can be acidified. Oxidized species like SO_4 and NO_3 could accumulate during the dry period in the upper soil layers and would be washed out during heavy rainstorms (Bechtold et al., 2003; Dillon and LaZerte, 1992; Eimers et al., 2007; Szkokan-Emilson et al., 2013; Zhang et al., 2010). Reoxidation of reduced S species was demonstrated for the wetland site in the Lehstenbach catchment (Alewell et al., 2006). Oxidizable sulphur originating from historical SO_4 deposition can lead to intensified acidification: the wetland receives anoxic groundwater from intermittent seeps and fens resulting in high amounts of Fe in the upper soil layers (Küsel and Alewell, 2004). In areas with a large Fe pool in the soil, historical SO_4 deposition strongly enhances FeS_x storage. An increased pool of FeS_x stimulates drought-related soil acidification, which influences the pH and causes an increase of potentially toxic metals like Al in pore water (Lamers et al., 1998). This relationship between acidification and Al release has been extensively investigated (e.g. Smolders et al., 2006; Szkokan-Emilson et al., 2013; Tipping et al., 2003; Watmough and Orlovskaya, 2015) and was in line with the high influence of Al-releasing weathering reactions found for Cluster 4.

4.4. Role of hydrological processes

In more than 80% of all cases, consecutive samples were assigned to the same cluster, pointing to rather stable biogeochemical conditions and only minor effects of hydrological processes in the short-term, i.e., within single stormflow events. This is in striking contrast to pronounced short-term chemical responses during stormflows observed in other streams of the catchment (Lischeid and Bittersohl, 2008; Lischeid et al., 2002; Strohmeier et al., 2013). However, in contrast to those streams, there is no well-buffered deep groundwater recharging the wetland stream that could be mixed in varying portions with near-surface runoff.

In winter, spring and early summer, runoff peaks did not change the cluster occurrence, i.e. the Moorbach stream water quality. This was true for a wide range of hydrological boundary conditions in the wetland, i.e. during water saturation conditions (April/May 2005, January 2007, April 2007) and after periods of extensive water level drawdown ($>$ 20 cm; April 2007; Fig. 6), once the water level had recovered to complete saturation. Thus, the magnitude of discharge and base flow or storm flow conditions seemed to play a negligible role, as illustrated by the wide range of discharge during sampling for Clusters 1, 2 and 3 (Fig. 7). This observation pointed to rather stable chemical conditions in the wetland due to low microbial activity, which was in line with the results of Olivie-Lauquet et al. (2001).

Runoff events after periods of moderate groundwater level drawdown (less than 15 cm) in summer and autumn did not have a systematic influence on the cluster occurrence during or after the event on stream water quality. In some events, a shift from either Cluster 2 to Cluster 1 (or vice versa) with a quick shift back was observed. Thus, precipitation events after periods of moderate groundwater level drawdown can result in a decline or a peak of solute concentration of only short duration.

In contrast, stormflow after periods of extensive groundwater level drawdown (more than 20 cm) in summer and autumn systematically induced cluster changes from either Cluster 2 or 3 to Cluster 4, i.e. a substantial change of the stream water chemistry due to flushing of solutes that accumulated during the preceding drought period. Cluster 4 was observed for up to 28 days or longer after the precipitation event. Thus, extensive drought periods seem to have generated a high NO_3 and SO_4 export from the wetland to the Moorbach stream, despite reduced

sulphur deposition, combined with Al release.

These non-linear relationships between biogeochemical and hydrological processes have to be taken into account to produce reliable predictions of solute export with hydrochemical models used for water management purposes, especially with regard to the expected increasing frequency of drought periods due to climate change.

The residence time of the water seems to play an important role for the biogeochemical transformation within the wetland. Indeed, biogeochemical transformation rates are discussed to depend on the ratio between residence and reaction time scales (Oldham et al., 2013). This needs to be taken into account with regard to the impact of wetlands on water quality in the receiving streams.

4.5. Implications for single solutes

The interplay between the hydrological boundary conditions and the biogeochemical processes in the wetland via the microbial activity in the wetland turned out to determine the different types of Moorbach stream water samples. This interplay will be demonstrated below for NO_3 (positively correlated with the first Isomap component), DOC and SO_4 (positively and negatively correlated with the second Isomap component, respectively) and Al (negatively correlated with the third Isomap component).

NO_3 concentration usually follows the annual cycle of water table depth with a spring maximum and an autumn minimum (Aubert et al., 2013a; Prior and Johnes, 2002; Sponseller et al., 2014). However, NO_3 export in our catchment showed a much more complex pattern. This was presumably due to the interplay between water table position and microbial activity: as reflected by the change from Cluster 3 to Cluster 2, NO_3 export decreased from April to May 2005, although the water table remained near the soil surface (Figs. 5 and 6), likely due to enhanced microbial activity. NO_3 concentration near the detection limit represented by Cluster 1 was not limited to autumn runoff events as observed by Prior and Johnes (2002), but occurred e.g. in June or August due to enhanced microbial activity during periods of moderate groundwater level drawdown in the wetland (Fig. 6), and consequently, longer water residence time (Fig. 7). Periods of extensive groundwater level drawdown (Cluster 4), however, led to NO_3 concentrations similar to those in early summer (Cluster 2), even in the autumn months (Fig. 6). Similarly, Lupon et al. (2016) observed that NO_3 release from riparian wetlands was correlated with riparian evapotranspiration. Thus, the interplay between biogeochemical and hydrological processes has important implications for estimating the effect of wetlands for NO_3 retention, and its NO_3-removing capacity, and has to be taken into account in water management strategies.

DOC peaks in storm flow were ascribed to near-surface runoff during storms (Hagedorn et al., 2000; Hornberger et al., 1994; Inamdar et al., 2011; Mitchell et al., 2006), i.e., in the layer of highest DOC production (Cole et al., 2002). In the wetland studied here, however, DOC concentration in runoff showed high variation, although runoff was generated mainly in the topsoil layer. The highest DOC concentration was found for stream water samples represented by Cluster 1, followed by those represented by Cluster 2 (Fig. 5). Cluster 1 was characterized by discharge of wetland waters with the highest influence of anoxic redox processes, followed by Cluster 2 (Fig. 4). In contrast, declining DOC concentration and high SO_4 concentration occurred after periods of extensive groundwater level drawdown as reflected by the shift to Cluster 4 (runoff events beginning in July 2005, August, September and October 2006; Fig. 6), despite the water table rising up to the soil surface and topsoil water discharging to the Moorbach stream. In fact, during phases of high water tables, iron reduction was favoured and led to a concomitant DOC release. In contrast, during drought periods DOC concentration declined in the pore waters of the riparian wetland under study (Knorr, 2012) and elsewhere (Juckers and Watmough, 2014). A pattern inverse to that for DOC was observed for SO_4 (Knorr, 2012). These observations for the pore waters seem to be reflected in the Moorbach stream water samples as well, indicating that solute export from the wetland to the Moorbach stream depends on the antecedent moisture conditions controlling biogeochemical processes like redox reactions in the wetland. It is remarkable that a corresponding anticorrelation between the historical SO_4 deposition and DOC has been found elsewhere (Ledesma et al., 2016) and on a larger scale (Monteith et al., 2007).

A positive correlation between Al concentration and discharge was described in several studies (Kirchner, 2003; Piatek et al., 2009; Stutter et al., 2001). However, in our study, no such correlation could be observed. Aluminum concentration differed significantly between Clusters 1 and 4 (Fig. 5), although discharge did not (Fig. 7). In addition, Clusters 1 and 3 represented the highest and the lowest Al concentration, coming along with low and high discharge values, respectively. The Al concentration increased from Cluster 3 to Cluster 1 (Figs. 5 and 8), i.e., from winter to the summer months, following a seasonal pattern rather than discharge patterns. A similar seasonal pattern was observed by Muller and Tankéré-Muller (2012) and was related to higher microbial activity in summer. Thus, biogeochemical conditions related to water table position and season rather than discharge were essential for Al release to the Moorbach stream. Consequently, in catchments with a high proportion of wetland area, high Al concentration can be expected not only episodically during runoff peaks after drought periods, but over a longer period during the summer months. Higher air temperatures due to climate change will likely amplify Al release from wetlands to streams with consequences for water management strategies.

5. Conclusions

A Cluster Analysis of water quality data from a small stream draining a riparian wetland helped better understand the interplay between hydrological and biogeochemical processes in the wetland. Cluster analysis allowed a more detailed classification then the general classification using the Piper and Schöller diagrams. Solute export seemed to depend on the interplay between water table position and seasonally-varying biological activity, and thus varying biogeochemical conditions in the wetland. Temporal variability of stream water quality during single runoff events was negligible. Minimum biological activity and short residence time in the wetland hardly altered the quality of the groundwater that discharged into the stream during the dormant season. In contrast, increasing biological activity and increasing residence time in spring and summer had a major impact on wetland and stream water quality.

Periods with extensive groundwater level drawdown of more than 20 cm and subsequent rewetting led to a substantial increase of solute concentration and load (NO_3, SO_4, Na, Al) that lasted for up to 28 days or longer. However, that effect seemed to depend crucially on the intensity of microbial activity during the preceding period of groundwater level drawdown, pointing to a substantial biogeochemical memory effect.

Similar results are expected with respect to the Cluster Analysis for catchments with comparable geology, climate, land use and wetland proportion, i.e., for catchments with comparable biogeochemical processes and residence time in the wetland. However, each factor or process influencing the biogeochemical processes in a catchment, like another geology or land use, can also influence the results of the Cluster Analysis. In addition, further research would be required to investigate the effect of different catchment sizes on the interplay between biogeochemical and hydrological processes in order to improve the understanding of biogeochemical and hydrological dynamics on different scales of interest.

It is concluded, that biological activity in the riparian wetland, interacting with water table dynamics, proved to be a primary determinant of stream water quality and solute export. These non-linear relationships should be taken into account in biogeochemical modelling for improving predictions of stream water chemistry in water resources

management. More than a shift of annual mean values, single dry and warm periods are likely to predominate the dynamics and thus limit the retention capacity of wetlands and enhance solute export to the streams. A sound understanding of these dynamics is a necessary prerequisite for assessing the impact of both climate and land use change on stream water quality, nutrient export and carbon sequestration in riparian wetlands.

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